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RESEARCH ARTICLE

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Synthesis, crystal structure and magnetic properties of single-molecule magnet: $[Mn_4(CF_3COO)_4(hmp)_6]$

Abstract The preparation, X-ray structure and magnetic properties are presented for a new mixed-valence tetranuclear manganese complex that functions as a single-molecule magnet (SMM): $[Mn_4(CF_3COO)_4(hmp)_6]$, where hmp^- is the anion of 2-(hydroxymethyl) pyridine and is a N,O bidentate chelate. The compound crystallizes in a monoclinic system, space group P_{21}/c (No. 14) with unit cell parameters $a = 13.663(3)$ Å, $b = 14.705(3)$ Å, $c = 14.734(3)$ Å, $\beta = 98.51(3)°$, $V = 2927.6$ Å^3 and $Z = 2$. The structure of the complex shows a novel coordination of the trifluoroacetate (TFA) anions, with one anion acting as a monodentate ligand while the second one coordinating through both oxygens to the same Mn center. Direct current magnetic susceptibility measurement in the 2–300 K temperature range supports a high-spin ground state. The presence of a frequency-dependent alternating current susceptibility signal indicates that the individual molecule is acting as magnet.

Keywords single-molecule magnet, manganese complex, synthesis, crystal structure, magnetic property

1 Introduction

Single-molecule magnets (SMMs) are an important class of compounds investigated in detail over the past decade for their potential applications in high-density magnetic storage media [1]. SMMs are formed of identical particles with well-defined size and shape and they can function as nanoscale magnets below a critical temperature. The phenomenon has been observed for polynuclear metal clusters that exhibit a large overall ground state spin value and a large axial zero-field splitting parameter. The combination of these factors produces an energy barrier between “spin-up” and “spin-down” states. In an external magnetic field their magnetic moments can be oriented, and when the external field is removed, the state is no longer possible by thermal activation at low temperature, and therefore slow magnetic relaxation is observed. Furthermore, quantum tunneling of the magnetization observed in SMMs renders them ideal candidates for the study of behavior at the quantum-classical interface [2].

Until now, the most studied family of SMMs are the dodecanuclear complexes of formula $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]^{n-}$ ($n = 0$, 1,2; $x = 3$, 4) [3–5]. Manganese clusters ranging in nuclearity from 2–84 [6–8] and a number of oxide-bridged clusters containing V [9], Fe [10], Co [11,12], and Ni [13] have also been shown to be SMMs. We herein describe the synthesis, crystal structure and magnetic properties of a new mixed-valence tetranuclear manganese single-molecule magnet.

2 Experimental

2.1 Instruments and reagents

All chemicals and solvents were used as received. The starting material $[Mn_{12}O_{12}(CF_3COO)_{16}(H_2O)_4]\cdot 2CF_3COOH\cdot 4H_2O$ was prepared according to the procedure based on the literature [14].

IR measurements were made on the sample pressed into KBr pellets in the 400–4 000 cm^{-1} region using a Nicolet 740 FT-IR spectrophotometer.

Magnetic susceptibility and magnetization susceptibility measurements were carried out with a Quantum Design SQUID magnetometer MPMSXL. DC magnetic measurements were performed with an applied field of 0.1 T in the 2–300 K temperature range. AC magnetic susceptibility measurements were performed in the 1.8–3.0 K range in a zero DC field and a 3×10^{-4} T AC field oscillating at

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frequencies in the 1–997 Hz range. The data were corrected for the diamagnetic contributions calculated from the Pascal constants.

Single-crystal X-ray data was collected on a BrukerSMART 1000 CCD X-ray diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.071073$ nm). The frames were integrated with the Bruker SAINT Software package and the data corrected for absorption using the program SADABS.

2.2 Synthesis of $[Mn_4(CF_3COO)_4(hmp)_6]$

A solution of $[Mn_{12}O_{12}(CF_3COO)_{16}(H_2O)_4]\cdot 2CF_3COOH\cdot 4H_2O$ (0.2 g) in THF (10 mL) was treated with hmpH (0.5 mL). The homogeneous reaction solution formed a light brown solution and a purple precipitate after being stirred for two days. The precipitate was collected by filtration, washed with a mixed solvent of THF-hexane and dissolved in MeCN to produce a red-brown solution. The solution was then filtered, followed by the slow diffusion of ethyl ether into the filtrate at room temperature to produce red-brown crystals. The crystals were collected by filtration, washed with ethyl ether and dried under vacuum. The overall yield of this product was ~19% based on the starting material $[Mn_{12}O_{12}(CF_3COO)_{16}(H_2O)_4]\cdot 2CF_3COOH\cdot 4H_2O$.IR(cm^{-1}): ν(C=O), 1676(s), 1639(s), 1607(s).

3 Results and discussion

3.1 Crystal parameters and description of the structure

Crystal parameters and basic information pertaining to data collection and refinement for the structure is summarized in Table 1. Selected bond distances and angles are listed in Table 2.

The molecular structure and the packing diagram of the title complex are provided in Fig. 1 and Fig. 2. As can be seen clearly, the molecular structure can be described as two Mn_3O triangular units fused along one edge. Each Mn_3 triangular unit is μ_3-bridged by an oxygen atom O(3) from hmp$^-$ and the edges of each triangular face consists of a μ_2-oxygen atom (O(1) and O(2)) from hmp$^-$. Nitrogen-oxygen containing chelates such as 2-(hydroxymethyl) pyridine (hmpH) are known to have a variety of possible binding modes, including bridging two, three, or four metals. It has been used for the synthesis of a number of Mn clusters, which have turned out to be SMMs [15,16]. Two TFA anions coordinate to Mn(2), one symmetrically bidentate and one monodentate. To the best of our knowledge, this is the first description of a tetranuclear complex having TFA anions mono- as well as dicoordinated to a manganese center.

Table 1 Crystallographic data and structural refinement parameters

formula	$C_{52}H_{52}F_{12}Mn_4N_6O_{16}$ formula weight	1 464.76
crystal system	monoclinic space group	$P2_1/c$ (No. 14)
a/Å	13.663(3) b/Å	14.705(3)
c/Å	14.734(3) α/(°)	90
β/(°)	98.51(3) γ/(°)	90
V/Å^3	2 927.6(10) Z	2
D_c/(g/cm^3)	1.662 F(000)	1484
crystal size/mm^3	0.19 × 0.24 × 0.28 temperature /K	110
θ range/(°)	1.5, 27.5 index range (h,k,l)	(−17/17, −18/19, −19/19)
Tot., Uniq.Data, R(int)	26 150, 6 637, 0.050 R, wR_2	0.0689, 0.1831
goodness-of-fit	1.054	

Table 2 Selected bond distances (Å) and angles (deg) for the title complex

Mn1 O1	1.874(3)	Mn2 O2	2.200(3)
Mn1 O3	1.991(3)	Mn2 O1	2.227(3)
Mn1 N2	2.064(3)	Mn2 N3	2.285(3)
Mn1 N1	2.200(4)	Mn2 O5	2.334(3)
Mn1 O3	2.223(3)	Mn2 O3	2.357(3)
		Mn2 O4	2.375(3)
O2 Mn1 O1	176.05(13)	O6 Mn2 N3	86.66(13)
O2 Mn1 O3	83.26(12)	O2 Mn2 N3	133.90(11)
O1 Mn1 O3	99.02(12)	O1 Mn2 N3	94.03(11)
O2 Mn1 N2	81.05(13)	O6 Mn2 O5	91.54(15)
O1 Mn1 N2	96.43(13)	O2 Mn2 O5	141.53(11)
O3 Mn1 N2	163.82(12)	O1 Mn2 O5	84.03(12)
O2 Mn1 N1	103.19(14)	N3 Mn2 O5	84.57(12)
O1 Mn1 N1	79.97(13)	O6 Mn2 O3	112.66(13)
O3 Mn1 N1	93.10(13)	O2 Mn2 O3	68.43(10)
N2 Mn1 N1	94.33(14)	O1 Mn2 O3	71.77(10)
O2 Mn1 O3	95.64(12)	N3 Mn2 O3	70.31(11)
O1 Mn1 O3	81.58(12)	O5 Mn2 O3	143.17(12)
O3 Mn1 O3	81.40(12)	O6 Mn2 O4	88.82(13)
N2 Mn1 O3	96.16(12)	O2 Mn2 O4	85.31(11)
N1 Mn1 O3	159.66(12)	O1 Mn2 O4	87.78(11)
O6 Mn2 O2	90.81(13)	N3 Mn2 O4	140.54(12)
O6 Mn2 O1	175.43	O5 Mn2 O4	56.37(11)
O2 Mn2 O1	91.96(11)	O3 Mn2 O4	145.48(11)

Most known SMMs contain Mn(III). This is due to the combination of a large number of unpaired electrons on each high spin, near-octahedral Mn(III) ion and the Jahn-Teller (JT) distortion that accompanies it, usually in the form of an axial elongation. The Mn centers were assigned formal charges of +3 and +2 on the basis of structural parameters. Mn(1) shows clear evidence of Jahn-Teller distortions, as expected for high-spin Mn^{III} in near-octahedral geometry, taking the form of axial

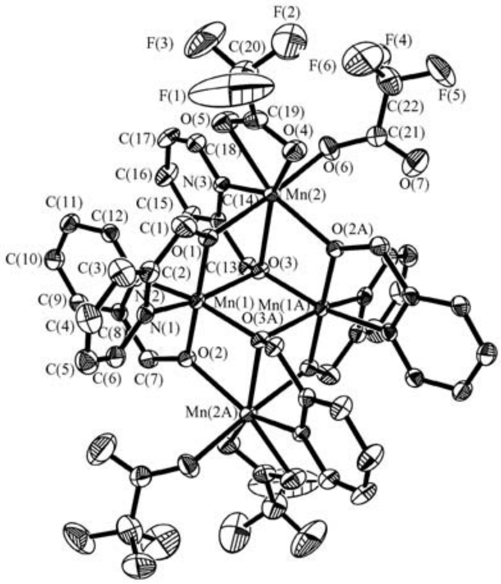

Fig. 1 View of the molecular structure of the title complex

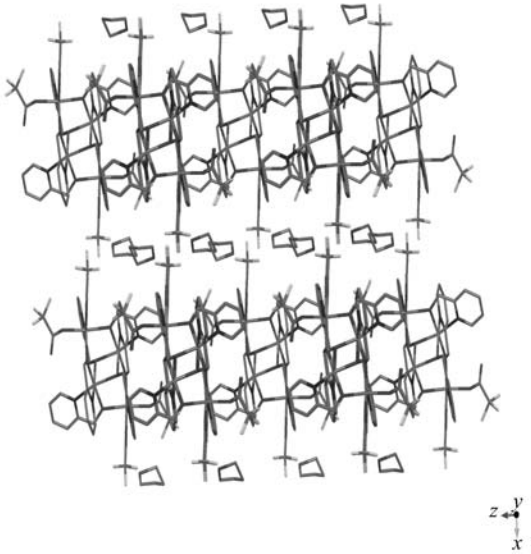

Fig. 2 Packing diagram of the title complex

elongation along the N(1)–Mn(1)–O(3). N(1)–Mn(1) (2.200 Å) and Mn(1)–O(3) (2.223 Å) are longer than the other four lengths (average 1.949 Å). The geometry at Mn(2) is a distorted pentagonal bipyramidal form, with O(1)–Mn(2)–O(6) being the axis. This type of seven-fold coordination is very unusual for manganese single-molecule magnet [17,18]. Mn(2) in the +2 oxidation level is supported by longer Mn-ligand bond lengths (average 2.277 Å) compared with those to Mn(1) (average 2.037 Å). Bond valence sum calculations (BVS) [19] were performed, and the obtained values of 2.94 for Mn(1) and 1.84 for Mn(2) confirm the Mn^{III} and Mn^{II} oxidation states, respectively.

3.2 Magnetic properties

DC magnetic susceptibility measurements were performed on crushed single crystals of the title complex in the temperature range from 2 to 300 K. As shown in Fig. 3, the $\chi_m T$ value at room temperature gradually increased as the temperature was decreased and reached a maximum value at 5.7 K, followed by a sudden decrease down to 1.8 K. This behavior indicates that the magnetic exchange interactions are ferromagnetic and the complex has a high-spin ground state $S = 9$ [17,20].

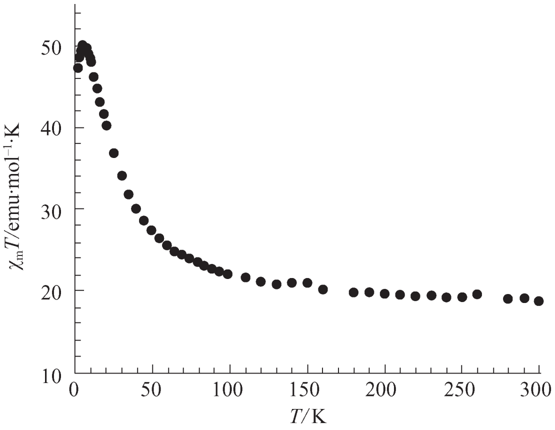

Fig. 3 Plot of $\chi_m T$ vs temperature for the title complex measured in a 1000 G dc magnetic field

In an AC susceptibility experiment, a weak field (typically 1–5 G) oscillating at a particular frequency is applied to a sample to probe the dynamics of the magnetization relaxation. If the magnetization vector can relax fast enough to keep up with the oscillating field, then there is no out-of-phase susceptibility signal (χ_m''). However, if the barrier to magnetization relaxation is significantly close to thermal energy, an out-of-phase AC susceptibility signal (χ_m'') is observed. In addition, the χ_m'' signal will be frequency-dependent. Frequency-dependent χ_m'' signals are an important indicator of SMMs. The obtained results for four frequencies are shown in Fig. 4. At temperatures below 3 K, a nonzero χ_m'' signal is observed, and this is frequency-dependent. Clearly, the peak maximum of these signals lie at temperatures < 1.8 K, the operating minimum of our instrument, and can not be observed. But the data suggests that the complex does indeed display the slow magnetization relaxation dynamics of a SMM.

4 Conclusion

A tetranuclear complex has been obtained from the reaction of $[Mn_{12}O_{12}(CF_3COO)_{16}(H_2O)_4]\cdot 2CF_3COOH\cdot 4H_2O$ with hmpH in THF. X-ray studies revealed that

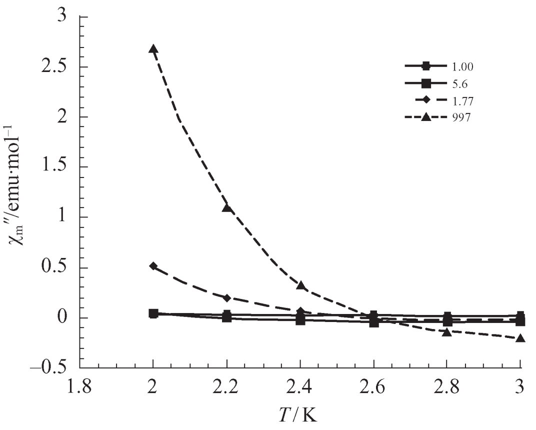

Fig. 4 Plot of the out-of-phase ac magnetic susceptibility signals vs temperature for the title complex

the trifluoroacetate ligands are coordinated to the Mn(2) center in a different mode: one is chelating and the other is monodentate. A frequency dependence of the out-of-phase AC magnetic susceptibility signal indicates that the complex is an SMM.

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